WHITE PAPER

BOOST OCTANE AND THROUGHPUT OF LIGHT NAPHTHA ISOMERIZATION UNITS USING DIVIDING WALL TECHNOLOGY

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Background of Isomerization:

Economic growth and environmental awareness across the globe required the refineries to produce clean and high-octane gasoline products.

The octane number or RON is primarily the knock resistance measure of gasoline. It has a numerical value from 0 to 100 and primarily describes the behavior of the fuel in the engine during combustion at lower temperatures and speeds.To take RON values to higher level,reforming and light naphtha isomerization process became an integral part of refineries. Light naphtha isomerization not only produces high octane isomerate products but it also takes care of the latest stringent gasoline specifications. Isomerization units can handle the benzene content of the gasoline pool and majority of benzene and its precursors are diverted to the light naphtha fraction as the feed to this unit.The isomerization unit saturates benzene to form cyclohexane. The configuration of an Isomerization unit depends on the required RON value of the gasoline pool.

Overview of light naphtha Isomerization unit

Isomerization and reforming are two processes which help in improving the octane barrel of the end product by either converting straight chain paraffins to their branched isomers or by changing linear hydrocarbons into branched alkanes & cyclic naphthenes which are then partially dehydrogenated to produce high-octane aromatic hydrocarbons respectively.

Isomerization reactions are reversible and mildly exothermic. The conversion to iso-paraffin does not reach completion since the reaction is equilibrium governed. Presence of other components in the feed such as benzene and naphthenes tend to raise the reaction temperature as benzene saturation and naphthene ring opening are highly exothermic reaction, while low temperatures favor the reaction of conversion of N- paraffins to isoparaffins. However, operating at low temperatures will decrease the reaction rate, so to overcome this a very active catalyst is usually employed.

Light naphtha isomerization is evaluated on the basis of the product yields and the RON of the isomerate product. The liquid product yield is determined principally by the extent of hydrocracking which takes in the isomerization unit. Hydrocracking is an undesirable side reaction which converts light naphtha into light hydrocarbon gas molecules which are low RON components. There is an inbuilt tendency in molecules with higher molecular number such as the heptanes and above to crack and produce undesirable components.C7+ molecules are diverted to the CCR unit instead of the Isom, and benzene and benzene precursors help this manage well. Figure 1 provides the primary light naphtha isomerization reactions.

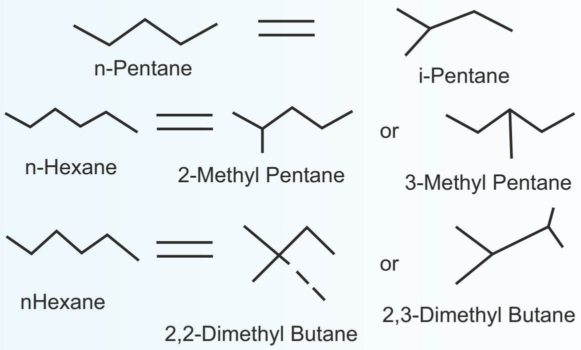


Figure 1: Primary reactions in light naphtha isomerization unit

The isomerization reaction enhances the octane values of straight chain alkanes by isomerizing the normal pentane nC5 (RON value of 62) to isopentane iC5 (RON of 93.5) .Other low RON components like,nC6 (RON 31) are isomerized to 2-methylpentane 2MP(RON 74) and 3-methylpentane 3MP (RON 76). These 2MP and 3MP molecules are then isomerized to 2,2 dimethylbutane (22DMB) with a RON of 94 and

2,3 dimethylbutane (23DMB) with a RON of 104. The table 1 below shows the comparative figures of the RON values of individual components in an Isomerization unit.

Components	Boiling Point °C	RON
Isopentane	27.8	99.5
N-pentane	36.1	61.7
2-2 Dimethylbutane	48.7	93
Cyclopentane	49.3	101.3
2,3 Dimethylbutane	58	104
2 Methylpentane	60.3	73.4
3 Methylpentane	63.3	74.5
N-Hexane	68.7	30
Methylcyclopentane	71.8	95
Benzene	80	> 100
Cyclohexane	80.7	83

Table 1 : RON values of individual components in a light naphtha isomerization unit

Isomerization unit configurations for meeting RON requirements:

As isomerization reactions are in equilibrium, various methods are used to push the reactions in the forward direction.The target RON desired for the combined isomerate product depends on two criteria, first being removal of products from the isomerate stream and other recycling back low octane molecules from the product back to the isomerization reactors. For this purpose, the Depentanizer and deisopentanizer are installed. It can be concluded that since the isomerization reactions are in equilibrium, the product octane number is defined by the number of separation units in the process. The sequence of columns used for separation of isopentanes or isohexanes clubbed with the isomerization unit with recycle give benefits on account of managing the equilibrium of the reactions taking place in the Isom unit so as to maximize RON.As the RON is increased there is an increase in reboiler duties which can be attributed to the following reasons:

- Increase in RON requires a sharp separation between low and high-octane molecules due to which the reboiler load of the column increases

- RON can also be increased by recycling back low RON components back to the reactor,which increases the reboiler duties of the downstream columns.

Apart from increased opex the capex involved in deploying various columns in the process of boosting octane makes the technocrats in the facility rethink on other options. Also, with facilities who have already invested in these columns, further enhancement of RON is always on the table. In the article to follow we will be discussing the various configurations of Isom unit.Figure 2 below shows the typical location of isomerization unit in a refinery. The top product from the Naphtha Splitter with C7 less than 3% is sent to the Isomerization unit.

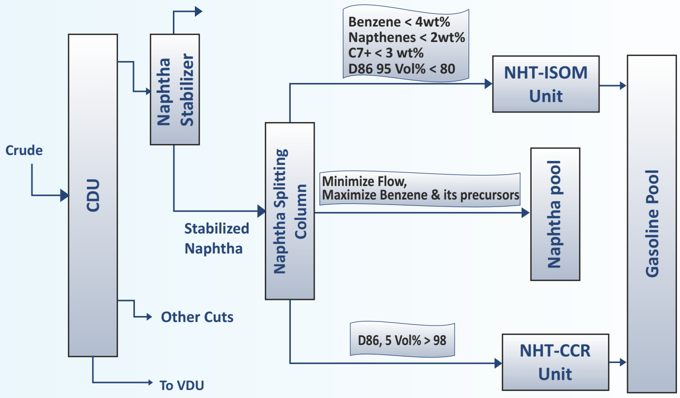


Figure 2 : Typical location of light naphtha isomerization unit in a refinery

Typical configuration of Isomerization units in a refinery:

Once Through vs hexane recycle Isomerization Units

The simplest Isom units are once through units. Fresh feed is sent to a feed pretreatment section and then passes through a series of Isom reactors after mixing with the hydrogen gas where it comes in contact with the catalyst. The reactor effluent is sent to a stabilizer column where hydrogen and light hydrocarbons produced due to hydrocracking are removed from the top as off gas and the isomerate is removed from the stabilizer bottoms. The RON achievable through these once through processes is about 85.

For refineries who looked forward to achieve RON beyond a value of 85 deploy ways to recycle low octane molecules back to the isomerization reactor. Facilities which have Isom reactor followed by a Deisohexanizer (DIH) column can achieve product RON of up to 88 by recycling a high percentage of the normal hexane, 2 methyl pentane and 3 methyl pentane which are low in RON back to the reactor.
This is achieved by drawing the mid-cut from the DIH column. The DIH produces a light isomerate distillate product consisting of C5's and branched C6 molecules (rich in DMBs), a C6 recycle side draw, and a C7+ bottoms product. For a recycle stream at 60% of the fresh feed an octane increase of several points is achieved compared to the once-through operation. Typically, one can expect a RON increase from 83-84 to 87-88 when DIH column hexane recycle to the isom reactor. Figure 3 provides typical configuration of light naphtha isomerization unit with hexane recycle.

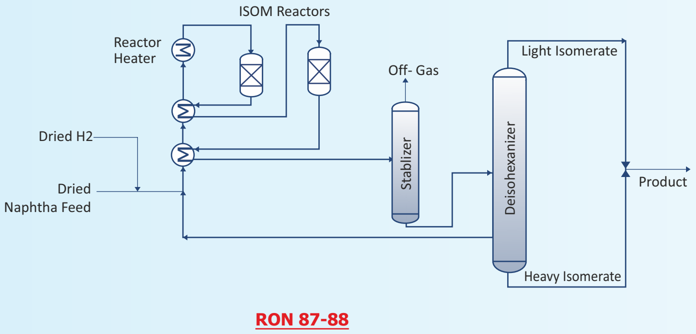


Figure 3 : Typical configuration of light naphtha isomerization unit with hexane recycle

Isomerization unit with hexane recycle and deisopentanized feed

Some facilities in addition to DIH column with recycle, have the deisopentanizer (DIP) column installed before the isom reactor. This helps in achieving an isomerate product of RON upto 90. As the DIP is placed in a feed fractionation section, it removes iC5 from the feed as overhead distillate product which pushes the reaction in the forward direction. The balance of the feed is sent to isomerization reactors and the reactor effluent is sent to a DIH column to separate high octane C5/C6 isomerate product from low octane C6 molecules which are recycled to the isomerization reactor. Thus the addition of a DIP as shown figure 4 increases the RON over that of a 'DIH only' configuration.

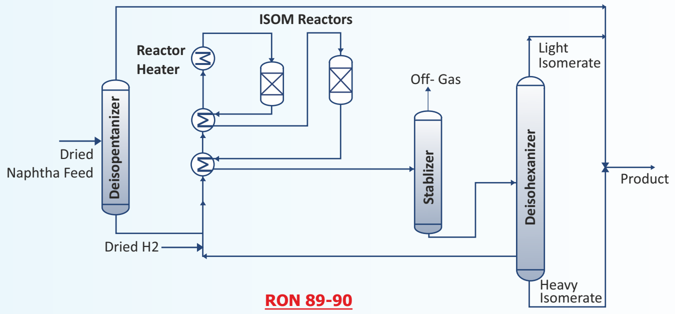


Figure 4 : Typical light naphtha isom. unit with hexane recycle & deisopentanized feed

Isomerization unit with hexane recycle, deisopentanized feed & C5 recycle

The unconverted normal pentanes with RON values as low as 61 are sent to the DIH distillate and thus becomes a part of final isomerate product. For full conversion of all normal paraffins, recycling normal paraffins is required via a Depentanizer (DP) installed before the DIH column. This helps to make a sharper separation between the DMB rich C6 isomerate product and the iC5/nC5 recycle stream. The DP column removes iC5/nC5 as an overhead distillate product upstream of the DIH and recycling it back to the deisopentanizer column, which in turn separates iC5 as the high RON top product & nC5 is recycled back to the reactor via bottoms product. This again helps in pushing the equilibrium reactions in the forward direction. The configuration shown in figure 5 improves RON upto 93.

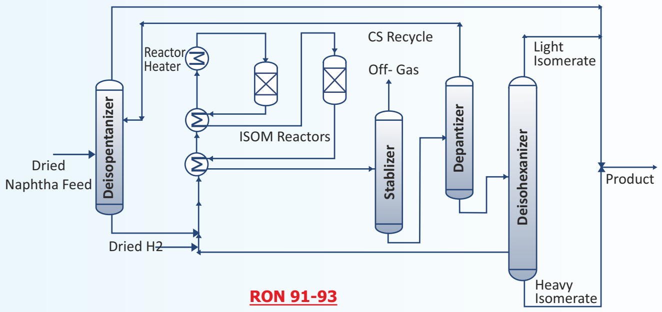


Figure 5 : Isomerization unit with hexane recycle, deisopentanized feed & C5 recycle

The table 2 below expresses explicitly that how the introduction of DP/DIP/DIH columns in the Isom loop in various combination clubbed with the type of process employed impacts the achievable RON.

Isomerization Unit Process Configuration	No of Column	RON of Isomerate Product
Once-through	Stablizer	81-84
Hexane recycle	Stablizer + Deisohexanizer	87-88
Deisopentanized feed and hexane recycle	Deisopentanizer + Stabilizer + Deisohexanizer	89-90
Pentane and hexane recycle	Deisopentanizer + Stabilizer + Depentanizer + Deisohexanizer	91-93

Table 2: Typical RON of various isomerization unit configurations

Developments in Dividing wall Technology and its use in Isomerization

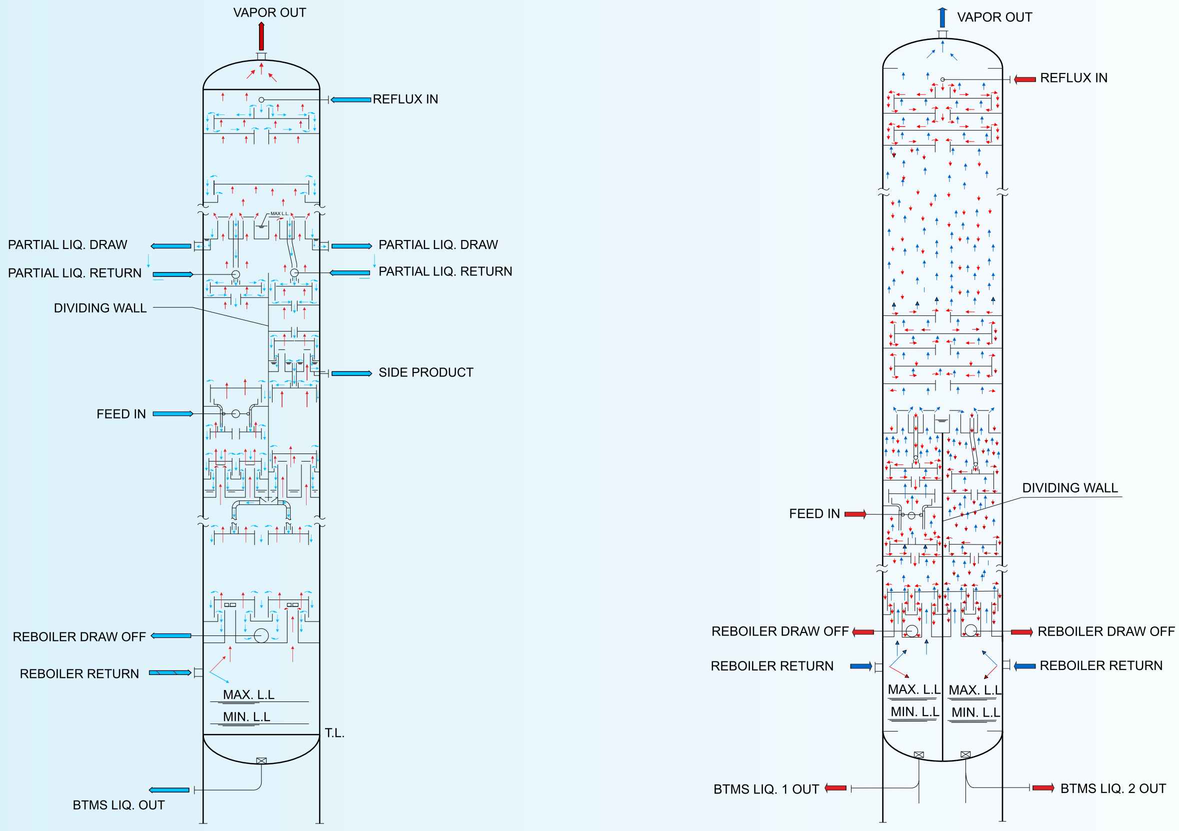
Advancements in distillation plays a key role in minimizing costs of new and revamped projects in a refinery. Dividing wall column technology is one of such advancements which had limited acceptance 20 years back and is now reshaping our distillation processes. Dividing wall column technology (DWC) is increasingly used to modernize conventional distillation sequences especially in revamps of existing units. Besides energy and throughput increase, DWC revamp significantly improve the performance of downstream units.As shown in the figure the alignment of the dividing wall inside the column plays a dominant role in the selection of DWC for a particular separation. The middle dividing wall column is an ideal alternative for side cut columns, which helps in increasing throughput and gives better product specifications. The top dividing wall column provides an additional source of heat integration with other process streams. On the other hand, the bottom dividing wall columns has an advantage of replacing two columns arrangement in an indirect sequence.

The latest advancement in the field of dividing wall columns is the Dual wall dividing columns which are known to have a higher thermodynamic efficiency than their counterparts. From outside it is no different from a simple dividing wall column but has the capability of delivering four or more high purity products from a single column. As Dual wall columns are robust, flexible and easy to operate this technology has become an extremely viable technology. Figure 6 provides elevation of commonly used dividing wall columns.

Revamp of DIH column using dividing wall column technology

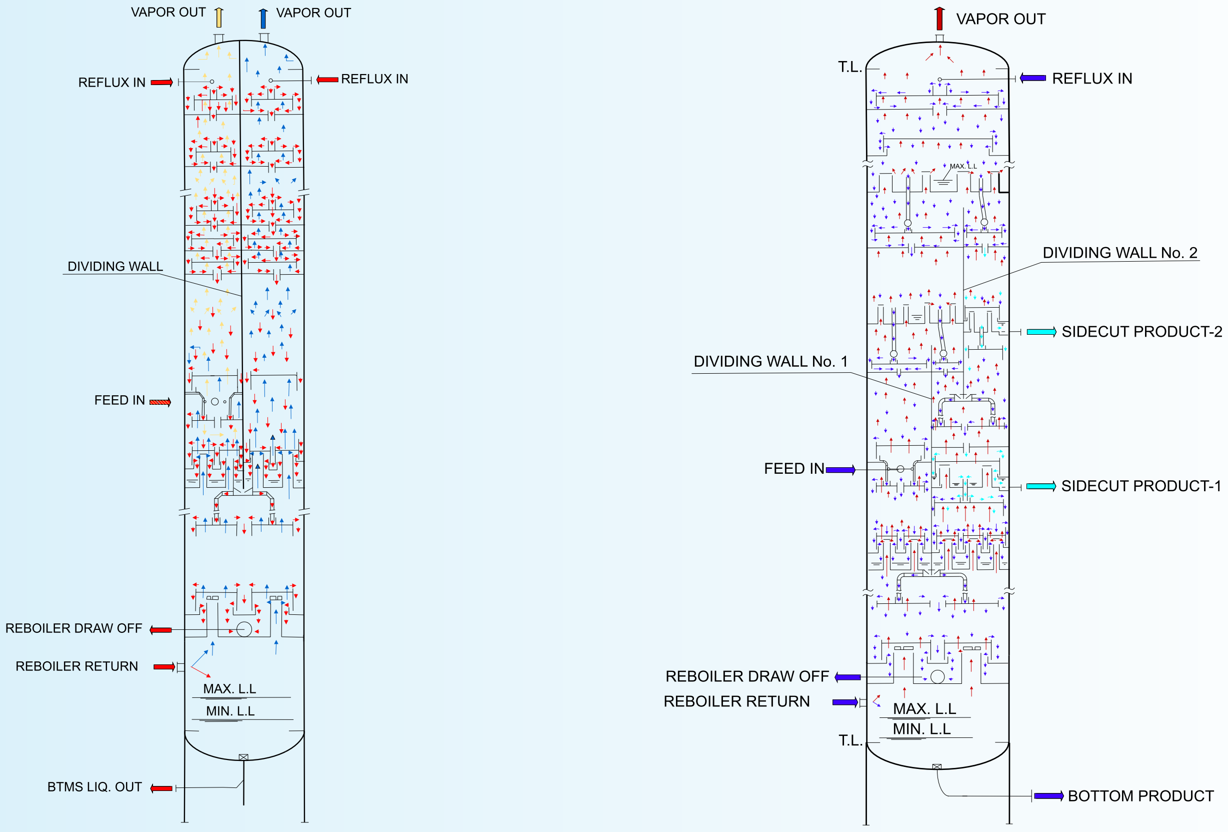
Dividing wallcolumn technology plays a key role in enhancing the performance of isomerization units. Facilities who look forward to improving the RON of the final isomerate, find divided wall column technology very lucrative as this involves only the deisohexanizer (DIH) column to be revamped,so as to include the additional functionality of deisopentanizer (DIP) or depentanizer (DP) columns as the case maybe. Besides enhancing the separation, DWC revamps provide considerable energy savings as compared to the conventional distillation column flow schemes. The use of DWC technology in isomerization unit not only targets improvement in RON but brings added advantage of increased throughput which would otherwise require installation of new columns. The remaining part of the article focusses on the applications and the outcomes of revamping the DIH column in various configurations discussed earlier in the article.

Application of DWC in Isom units with hexane recycle:The DIH column recirculates the unbranched molecules mainly n-hexanes and methyl pentanes after removal of the branched high RON molecules back to the Isom reactor. The top product ie the light isomerate mainly contains isopentanes, dimethyl butanes and methyl pentanes. The lesser the amount of methyl pentanes going to the top product the better the RON



MIDDLE DIVIDING WALL COLUMN

BOTTOM DIVIDING WALL COLUMN



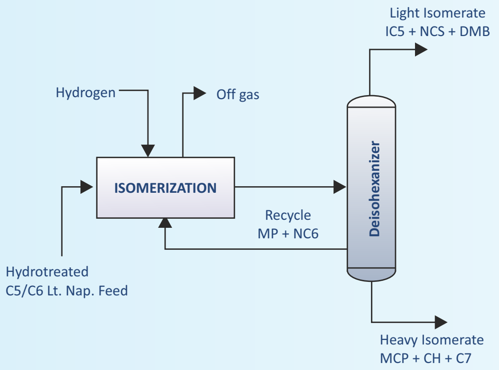
TOP DIVIDING WALL COLUMN

DUAL DIVIDING WALL COLUMN

Figure 6: Elevation of commonly used dividing wall columns

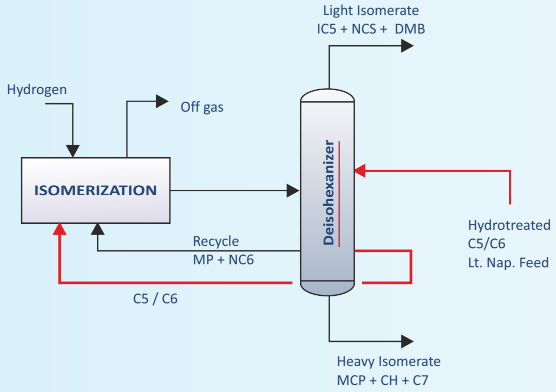
value of the final isomerate. Though this configuration definitely gives higher RON than once through process, the RON can be further increased by recirculating the methyl pentanes back to the reactor.

Isom Unit with DIH Recycle



RON 87-88

Revamp of DIH Column to DWC Prime



RON 89-90

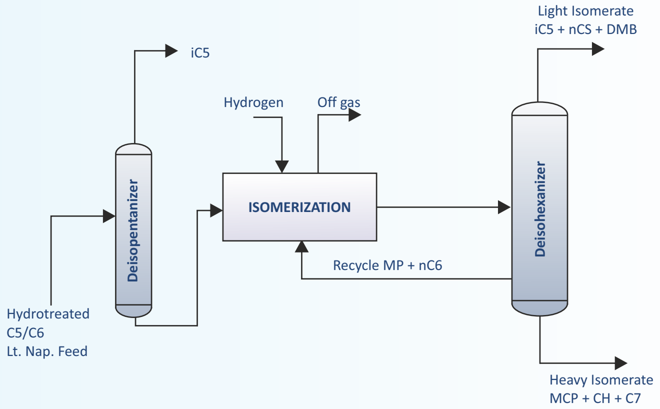
Figure 7 : Revamp of DIH column to DWC in Isomerization unit with hexane recyle

Also, separation of isopentanes present in the fresh feed going to the isomerization reactor contribute to higher RON values. The isopentanes present in the fresh feed take a free ride in the isomerization reaction process and restrict the forward reaction to produce more branched chain components. The traditional method of removing isopentanes from fresh feed is to install a deisopentanizer column upstream of the isomerization reactor.

There vamp of existing DIH column to a dividing wall column enables it to have a dual functionality of a deisopentanizer. Hydrotreated Naphtha is first sent to the revamped DIH column which now produces foursharp cuts. As shown in the figure 7 the light/heavy isomerate and the recycle are managed in the similar manner as before the revamp,while fourth cut ie. the fresh feed to the isom reactor without the Isopentanes. This is an attractive and lucrative scheme as dividing wall column revamp of DIH saves the installation of a DIP column though offering the benefits of the same.

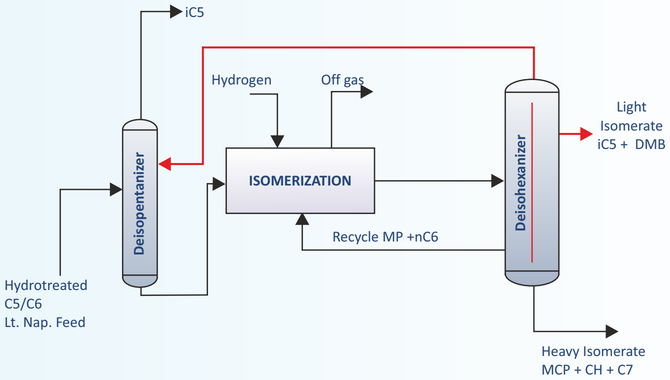
The advantage by this revamp is boost in RON to 90 as against 87 along with a fresh feed increase of 10-20%. The figure 7 shows the comparison between the conventional and post revamp of DIH to dividing wall column configuration unit with hexane recycle.

Isom with DIP & DIH Recycle



RON 89-90

Revamp of DIH Column to DWC Prime



RON 91-93

Figure 8: Revamp of DIH column to DWC in Isomerization unit with hexane recycle & deisopentanized feed

Conventional Configuration of Isom with hexane recycle and DIP column are able to attain RON close to 90 as the presence of DIP column helps in removing majority of i-C5 before the reactor which effects the reaction equilibrium in the forward direction. But to achieve RON values beyond this number, unreacted nC5's needs to be recirculated back to the reactor. As the DIH column in the conventional configuration is not able to restrict n-C5 going to the light isomerate hence maximum conversion of n-C5 to its high-octane isomer is not achieved.Also, because some portion of n-C5 becomes a part of the light isomerate it effects the RON adversely. By revamping the conventional DIH column to dividing wall more sharper cuts can be obtained and RON of the isomerate can be improved further.

As shown in figure 8 to improve the RON of the final product further the DIH column is revamped to a dividing wall column so as to draw four cuts out from the column. The light and the heavy isomerate are combined and send to the gasoline pool, while the third cut is recycled to the reactor in similar manner as in the conventional scheme.The fourth cut drawn from the DIH column primarily consists of iC5 along with unreacted nC5's which is recycled back to the DIP column. The deisopentanizer column removes isopentanes from the fresh feed along with the recycle stream from the revamped DIH DWC column. The bottoms of the DIP column are rich in straight chain components and is routed to the Isom reactor.The revamp of DIH column in this configuration provides a dual functionality of a DP column too and helps in achieving RON anywhere between 91-93 of the final isomerate product.

The table 3 below summarizes the benefits of dividing wall column for various isomerization configurations.

No of Column in Isomerization unit configuration	RON of Existing Isomerization Unit	Performance of isomerization unit after revamp of deisohexanizer column to dividing wall column		
		RON	Increase in throughput	Remarks
Stabilizer + Deisohexanizer (DIH)	87-88	89-90	10-20%	Existing DIH column performs dual functionality of hexane recycle & deisopentanizer after the revamp to DWC
Deisopentanizer (DIP + Stabilizer + Deisohexanizer (DIH)	89-90	91-93	5-10%	Existing DIH column performs dual functionality of hexane recycle & Depentanizer after the revamp to DWC

Table 3: Performance of Isomerization unit after revamp of DIH column to DWC

Conclusion

The benefits of dividing wall technology have grown beyond reduction in energy or capex. Refineries are using DWC technology for maximizing revenue from newer or better products. DWC's are increasing used in debottlenecking existing units in the refinery.Light naphtha isomerization is one such example, in which a simple revamp of DIH column improves the unit's performance by improving the RON along with an increase in throughput.